

519,711

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



30 DEC 2004



(43) International Publication Date
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number
WO 2004/005572 A1

- (51) International Patent Classification⁷: **C22C 38/50**, 38/52, C23C 8/26
- (21) International Application Number: PCT/SE2003/001159
- (22) International Filing Date: 2 July 2003 (02.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0202107-9 3 July 2002 (03.07.2002) SE
- (71) Applicant (*for all designated States except US*): SANDVIK AB [SE/SE]; S-811 81 Sandviken (SE).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): BERGLUND, Göran [SE/SE]; Odengatan 24, S-811 34 Sandviken (SE).
- (74) Agent: ZIEHE, Gabriele; Sandvik AB, Intellectual Property, S-811 81 Sandviken (SE).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SURFACE MODIFIED STAINLESS STEEL

(57) Abstract: The present invention relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv and which is in form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries, particularly useful in applications with high demands on a combination of high strength and/or toughness and wear resistance and as substrate for coating.



WO 2004/005572 A1

SURFACE MODIFIED STAINLESS STEEL

FIELD OF THE INVENTION

- 5 The present invention relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv and which is particularly useful in applications with high demands on a combination of high strength and/or toughness and wear resistance and as substrate for coating.

10 BACKGROUND OF THE INVENTION

Stainless steel alloys are relatively less hard than other steel materials. As a result in many applications the stainless steel article or part is provided with a hardened surface, often referred to as case hardening. The concept of case
15 hardening is to transform a relatively thin layer of material at the surface of the part by enrichment of carbon or other ingredients to make the surface harder than the matrix of the alloy, where matrix is the of the surface modification unaffected part of the steel. The steel thus retains in bulk the desired formability of stainless steel without the softness of the matrix at the surface of modified
20 steel.

Stainless steels are often casehardened by carburization. Carburization is a process by which carbon atoms are diffused in solution into the surface of the article. Known case hardening processes are performed at high temperatures. However, carburization processes performed at temperatures greater than
25 about 540°C (for stainless steel alloys) can promote the formation of carbides in the hardened surface.

Plasma nitriding is an alternative case-hardening process, which is carried out in a glow discharge in a nitrogen gas-containing mixture at a pressure of 100 to 1000 Pa (1 to 10 mbar), is one of the used method to treat stainless steel
30 surfaces, resulting in a nitrogen diffusion layer having high hardness and excellent wear resistance. Nitriding hardening is induced by the precipitation of nitrides in the surface layer.

DESCRIPTION OF THE RELATED ART

Plasma nitriding is the most recently developed surface hardening procedure.

5 The process replaces traditional nitriding methods, such as gas nitriding and nitrocarburation (short-term gas nitriding, bath nitriding and tenifer treatment) as identical thermo-chemical conditions can be established in this process. Plasma nitriding achieves higher hardness and wear resistance, while creating lower distortion.

10 Plasma nitriding is very cost effective. This is due to the fact that subsequent machining, finishing and residue-removal processes are frequently not required. Similarly, supplementary protective measures, such as burnishing, phosphatizing etc., under some conditions even galvanizing and hard-chrome plating, may not be necessary.

15 Plasma nitriding is performed in a vacuum furnace. Treatment temperatures in the range of 400 to 580°C are employed subject to the requirements of the process at hand. Typical treatment temperatures are in the range of 420 to 500 °C. The most commonly used process gases are ammonia, nitrogen,
20 methane, and hydrogen. Oxygen and carbon dioxide are used in the corrosion-protective step of post-oxidation. Aside from the type of process gas used, pressure, temperature, and time are the main parameters of the treatment process. By varying these parameters, the plasma nitriding process can be fine-tuned to achieve the exact desired properties in any treated component.

25 Any iron-based material can be subjected to plasma nitriding. The process does not require the use of special types of nitriding steel.

The results achieved through plasma nitriding can be reproduced with pinpoint accuracy. This is especially important in the manufacture of serial products.

30 US 5,632,826 discloses a precipitation hardened martensitic alloy in which the strengthening is based on the precipitation of particles. The strengthening particles have a quasicrystalline structure, said structure being essentially

obtained at aging times up to 1000 h and tempering treatments up to 650°C. This strengthening involves an increase in tensile strength of at least 200 MPa. It has now surprisingly been found that if steel according to US 5,632,826 is nitrided on the surface, an unexpected further increase in surface hardness is
5 obtained in difference to the matrix of said stainless steel.

SUMMARY OF THE INVENTION

It is therefore a primary object of the present invention to provide a stainless
10 steel alloy characterized by increased hardness at the surface of said alloy after modification of the surface at the same time as the hardness of the matrix of the stainless steel is also increased.

Another object of the invention is to provide products made of said surface modified stainless steel.

15 An additional object of the present invention is to provide a stainless steel substrate for coating with wear resistant layers.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Fig. 1 shows a light-optical micrograph of the microstructure of one sample of the surface modified stainless steel according to the present invention in 500X, where A is the nitrided surface layer, B is the stainless steel matrix.

Fig. 2 shows the hardness (in Hv) plotted over the depth (in mm) from the
25 surface.

DETAILED DESCRIPTION OF THE INVENTION

The stainless steel substrate before surface modification according to the present invention has the following composition (in weight-%):

5	Carbon	max 0.1
	Nitrogen	max 0.1
	Copper	0.5 - 4
	Chromium	10 - 14
10	Molybdenum	0.5 - 6
	Nickel	7 - 11
	Cobalt	0 - 9
	Tantalum	max 0.1
	Niobium	max 0.1
15	Vanadium	max 0.1
	Tungsten	max 0.1
	Aluminum	0.05 - 0.6
	Titanium	0.4 - 1.4
	Silicon	max 0.7
20	Manganese	≤ 1.0
	Iron	balance

and normally occurring usual steelmaking additions and impurities.

Said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

Plasma nitriding is a surface hardening process, which utilizes the properties of gas plasma, i.e. an ionized gas, to achieve desirable mechanical properties at the surface of the work piece.

30

The main influential parameters in nitriding are pressure, temperature, and time of treatment as well as the chemical composition of the ionized process gas.

Plasma nitriding takes place at a vacuum pressure between 0.3 to 10 mbar. The actual treatment pressure chosen is governed by the geometry of the part and the desired surface layer structure.

The treatment temperature in the range of 400 to 580°C is selected according to the type of material and pre-treatment of the part and the desired layer structure. Treatment time varies between 10 minutes and 70 hours, and depends on the part to be treated as well as the desired structure and thickness of the layers formed. Plasma nitriding uses ammonia or gas mixtures containing methane, nitrogen, and hydrogen as the process gas. The process gas used is selected subject to the nature of the part to be treated and the required layer structure.

The invention also relates to a material treated with the method according to the present invention in form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or toughness and wear resistance, such as e.g. wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like.

EXAMPLE

The substrate as described earlier was subjected to a surface modification by a plasma nitriding process at 450 to 580°C during a period of time of 1 to 40 hours. This process obtains a hardening of the surface between 0.05 and 0.5mm. The hardening process can be carried out on wire, plate, strip, tube and pipe and parts with a wide variation of geometries, especially complex geometries. It is a special advantage of the stainless steel substrate used according to the present invention, that very complex geometries can be formed without any changes in dimension. The hardness of the surface is at least twice

the hardness of the substrate 0.5mm into the matrix. It is at 1200 Hv, preferably at least 1100 Hv.

Figure 1 illustrates the hardness profile from the surface of the substrates into the matrix. It has unexpectedly shown that the hardening effect is visible down
5 to 0.5 mm into the matrix. It is therefore considered being a big advantage of this combination of substrate and the method of surface treatment, that creates a surface modified material with a deep-hardened surface zone.

Thus, the surface modified stainless steel according to the present invention is
10 particularly well suited for use as substrate for the deposition of a wear resistant coating.

15

20

25

30

Claims

1. Stainless steel with a composition as following (in weight-%):

5	Carbon	max 0.1
	Nitrogen	max 0.1
	Copper	0.5 - 4
	Chromium	10 - 14
	Molybdenum	0.5 - 6
10	Nickel	7 - 11
	Cobalt	0 - 9
	Tantalum	max 0.1
	Niobium	max 0.1
	Vanadium	max 0.1
15	Tungsten	max 0.1
	Aluminum	0.05 - 0.6
	Titanium	0.4 - 1.4
	Silicon	max 0.7
	Manganese	≤ 1.0
20	Iron	balance

Normally occurring usual steelmaking additions and impurities

characterized in, that said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

25 2. Stainless steel according to claim 1, characterized in, that said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

30 3. Method for the making of a surface modified stainless steel according to claim 1, characterized in, that said stainless steel is subjected to a nitriding process at 450 to 580°C during a period of time of 1 to 40 hours in a plasma nitriding atmosphere.

4. Product according to any of the previous claims in form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or toughness and wear resistance, such as e.g. wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like and without change in dimension.

5. Material according to claims 1 and 2 use a substrate for the deposition of wear resistant coating.

15

20

25

30

1 / 1

Figure 1

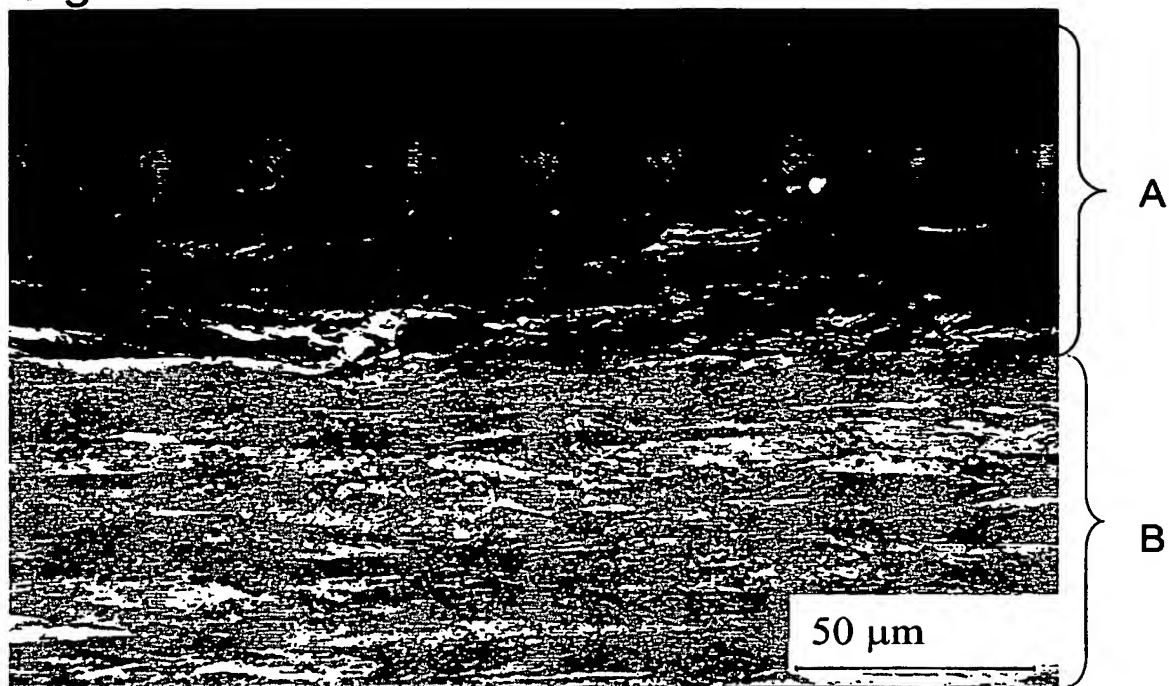
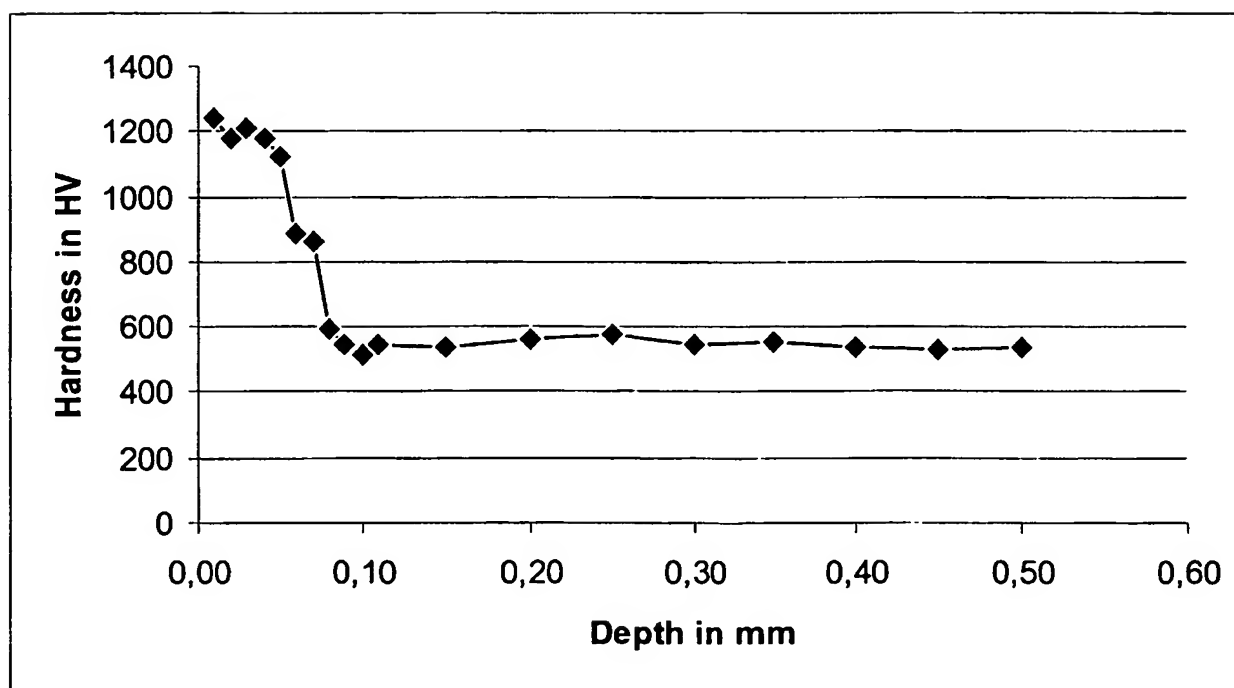


Figure 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 03/01159

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 38/50, C22C 38/52, C23C 8/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22C, C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5632826 A (ANNA HULTIN-STIGENBERG ET AL), 27 May 1997 (27.05.97), table, column 2 --	1-5
Y	GB 2364530 A (ALSTOM POWER N V), 30 January 2002 (30.01.02), page 4, line 29 - page 5, line 2; page 5, line 20 - line 22; page 5, line 9 - page 6, line 11 -- -----	1-5

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

19 Sept 2003

Date of mailing of the international search report

22-09-2003

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Anna-Maj Magnusson/MP

Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

26/07/03

International application No.

PCT/SE 03/01159

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
US	5632826	A	27/05/97	AU	687453	B	26/02/98
				AU	7827194	A	01/05/95
				BR	9407764	A	11/03/97
				CN	1043663	B	16/06/99
				CN	1134729	A	30/10/96
				DE	69425977	D,T	25/01/01
				EP	0722509	A,B	24/07/96
				ES	2150502	T	01/12/00
				JP	3321169	B	03/09/02
				JP	9504574	T	06/05/97
				RU	2135621	C	27/08/99
				SE	508684	C	26/10/98
				SE	9303280	A	08/04/95
				US	5759308	A	02/06/98
				WO	9509930	A	13/04/95
				ZA	9407707	A	06/02/96
GB	2364530	A	30/01/02	GB	0115200	D	00/00/00
				CA	2351286	A	21/12/01
				EP	1270759	A	02/01/03
				GB	0015025	D	00/00/00
				US	2002014208	A	07/02/02